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# Silanization of quartz, silicon and mica surfaces with light-driven molecular motors: construction of surface-bound photo-active nanolayers†‡

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The attachment of molecular rotary motors containing triethoxysilane functional groups to quartz, silicon and mica surfaces is described. Motors containing silane coupling agents in their structure form stable molecular layers on quartz and silicon surfaces. Motors attached to these surfaces were found to undergo photochemical and thermal isomerization steps similar to those observed in solution. Additionally, successful formation of molecular "carpets" on atomically flat mica extending micrometer-sized length scales is presented. These "carpets" were found to undergo morphological changes upon irradiation with UV-light.

## Introduction

Stimuli-responsive molecular assemblies are an exciting class of materials in nanotechnology research.<sup>1–8</sup> A major challenge is to use these systems to perform work.<sup>9</sup> One approach towards this goal is the assembly of molecules capable of undergoing controlled structural changes on a solid surface and using their collective action to induce nano- or macroscale movement.<sup>10–13</sup> It has been demonstrated that thin films of stimuli-responsive molecules are able to alter the wettability of a surface,<sup>12,14</sup> control the organization of liquid crystal layers<sup>15–17</sup> and control cell adhesion<sup>18</sup> via structural changes triggered by external cues. Systems that can be controlled by light are of particular interest due to their non-invasive nature, fast response times and the compatibility of light with a variety of solid materials.<sup>10,12</sup> Many of the reported self-assembled monolayers (SAMs) containing switchable molecules are prepared on silicon-based materials because of their relevance to molecular electronic devices,<sup>19–21</sup> relatively low price and chemical, mechanical and thermal stability. Preparation of SAMs on silicon and quartz allows for the construction of robust, covalently-bound molecular layers that can be analyzed with a range of routine characterization techniques such as UV-vis, CD and IR-spectroscopy. Exploring the self-assembly of dynamic and stimuli-responsive molecular

systems along with their behaviour in the confined environment of a surface-bound monolayer is relevant to the development of functional molecular devices.

Molecular motors based on overcrowded alkenes provide promising photon-driven systems.<sup>22</sup> Their ability to undergo controlled unidirectional rotation while being attached to solid surfaces,<sup>23–26</sup> and the wide range of speeds at which they are capable of rotating<sup>27–29</sup> make them attractive candidates not only to control surface properties but also to control the motion of nano- or micrometer scale adsorbed materials.<sup>30</sup> The synthesis of molecular rotary motors containing alkoxy-silane functional groups allows for their attachment to a variety of surfaces, most notably piranha-cleaned SiO<sub>2</sub>/Si, glass and quartz. Other high-energy surfaces that support the self-assembly of molecules with silane-based functional groups include aluminum oxide, germanium oxide, gold, glass and mica.<sup>31</sup> Mica, a sheet silicate, is of particular interest because it provides an atomically flat surface, facilitating atomic force microscopy (AFM) studies of adsorbed materials and the morphology of the SAM.

## Results and discussion

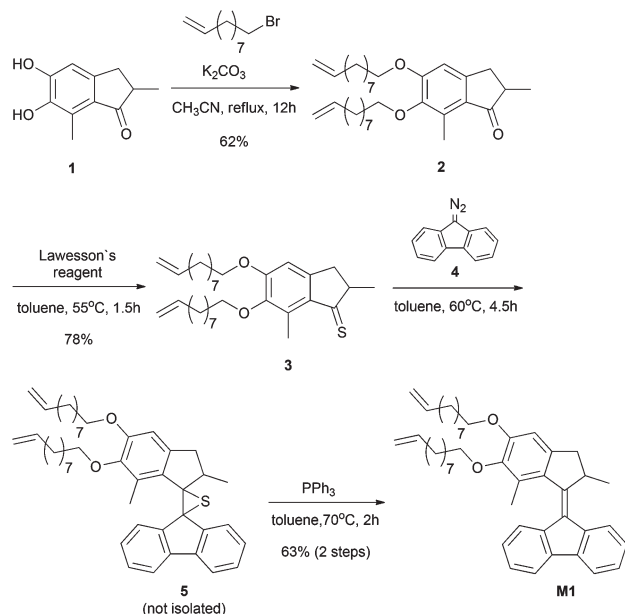
Molecular motor **M1** was synthesized containing two terminal double bonds (Scheme 1) (ESI†), which could be functionalized with triethoxysilane anchoring units (Scheme 2) making it suitable for attachment to Si–OH terminated surfaces (quartz and silicon wafers cleaned with piranha). Molecules containing a triethoxysilane-moiety are known to be relatively stable towards polymerization, and a variety of these compounds are commercially available and commonly used as silane coupling agents. As in the case of structurally similar

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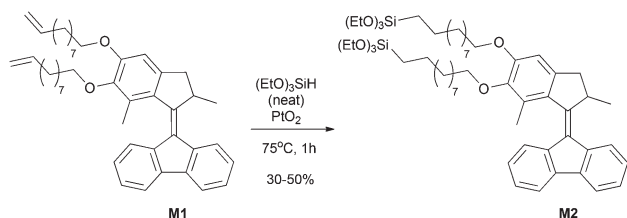
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†Electronic supplementary information (ESI) available: Detailed experimental procedures for the synthesis of alkenes **M1** and **M2** with characterization and spectra. See DOI: 10.1039/c3ob40276b

‡This paper is in honour of Professor Andrew Hamilton celebrating his 60th birthday.



**Scheme 1** Synthesis of dialkene-terminated motor **M1**.

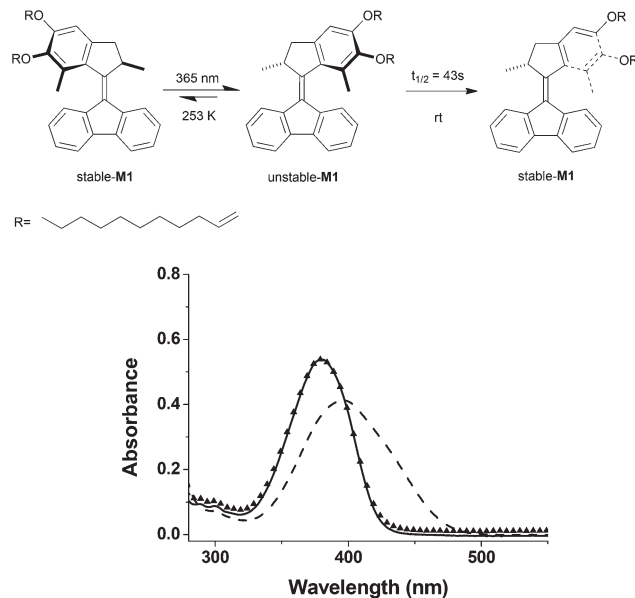


**Scheme 2** Synthesis of molecular motor **M2** containing triethoxysilane functional groups.

motors,<sup>33,34</sup> irradiation of **M1** resulted in an attenuation and red-shift of the absorption band at 379 nm to a broader band at 397 nm (Fig. 1). The shifted absorption band indicates the formation of a higher energy intermediate (unstable-form),<sup>35</sup> which was subsequently reconverted to the stable form upon warming the sample to rt. The recovery of the original absorption band upon warming is indicative that the thermal isomerization step is taking place.

The rate of conversion to stable-**M1** could be monitored by UV-vis spectroscopy. After the thermal isomerization at different temperatures (268, 263, 258 K) the Eyring-plot was constructed and the Gibbs free energy of activation ( $\Delta^\ddagger G^\circ$ ) of 81.8 kJ mol<sup>-1</sup> was calculated. By extrapolation, we calculated that **M1** has a half-life ( $t_{1/2}$ ) at rt of 43 s. Low-temperature <sup>1</sup>H NMR measurements revealed a photostationary state of stable-**M1**: unstable-**M1** of 2 : 1 (ESI<sup>†</sup>).

A platinum oxide (PtO<sub>2</sub>) catalyzed hydrosilylation reaction was chosen to convert the terminal double bonds of **M1** to silanes (Scheme 2). In a previous study<sup>36</sup> PtO<sub>2</sub> was found to be an efficient hydrosilylation catalyst for terminal alkenes with highly reproducible results and easy removal of the catalyst after the reaction.



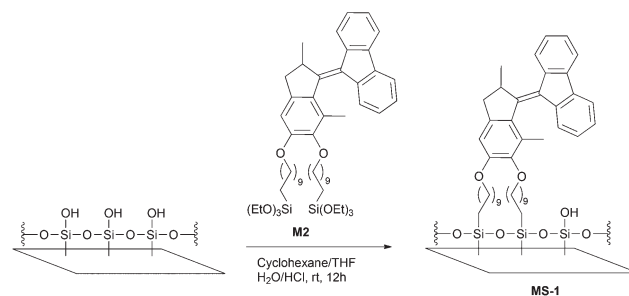
**Fig. 1** The stable form of **M1** (solid line) undergoes photoisomerization (dashed line) upon irradiation with UV-light ( $\lambda_{\text{max}} = 365$  nm) (MeOH, 253 K). The original spectrum is restored upon warming the sample to room temperature (▲).

The product disilane **M2** was found to be stable towards polymerization even during flash chromatography using silica gel as a stationary phase. Although polymerization was not observed (no precipitation or broadened absorptions in the <sup>1</sup>H NMR spectra were observed), partially hydrolyzed silanes were present in the crude reaction mixture and possibly form during purification as well. It is possible that the presence of free silanol groups contributes to the varying isolated yields due to their different interactions with the stationary phase (which could also include covalent attachment) during column chromatography.

### M2 on quartz and silicon surfaces

It was expected that disilane-derivative **M2** can be used for controlled surface functionalization (Scheme 3).

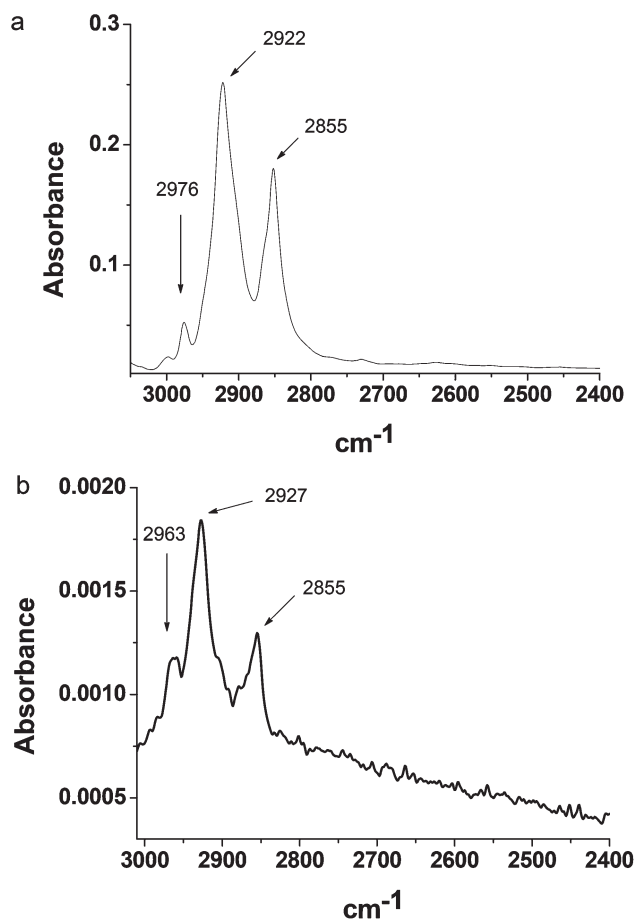
Pirahna-cleaned quartz and Si surfaces were immersed into a 1–10 mM solution of **M2** for 12 h. After removing from the self-assembly solution, the surfaces were rinsed by sonication



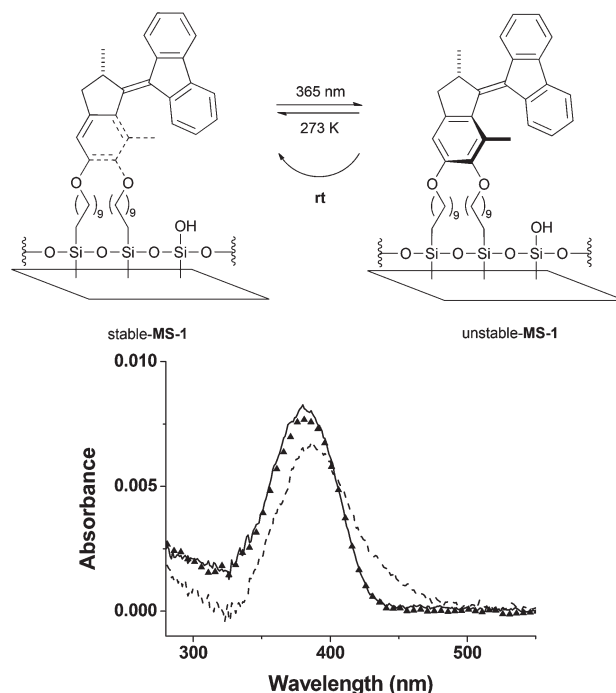
**Scheme 3** Attachment of triethoxysilane-containing motor **M2** to quartz and silicon surfaces.

in fresh DMF, toluene and methanol (2 min each) (see also the Experimental section). Successful assembly of **M2** was characterized by a variety of surface analytical techniques. The first indication of successful surface modification was obtained by water contact angle measurements. Since bare quartz and silicon are high energy surfaces, exhibiting complete spreading of water, any modification with an organic group is expected to induce a change in this value. Indeed, the surfaces treated with motor **M2** showed a large increase in the contact angle from 0° (complete wetting) to 87(±2)°. Ellipsometry was used to measure the thickness of the SAM. We obtained thickness values of 2.0(±0.2) nm in agreement with the calculated length of 2.1 nm of motor **M2** indicating the formation of a monomolecular layer.

Further evidence of the presence of **M2** on the surface was confirmed by ATR-FTIR spectroscopic measurements. Chemical identification of **M2** on the surface is evident by the appearance of the CH<sub>2</sub> and CH<sub>3</sub> stretching modes at 2855, 2927 and 2963 cm<sup>-1</sup> in the IR-spectra which is similar to the IR absorptions of a bulk sample of motor **M1** in the same region (Fig. 2). Note that these stretching modes do not appear when bare Si/SiO<sub>2</sub> is measured.



**Fig. 2** ATR-IR spectra of motor **M1** (a) and **MS-1** (b). The presence of the motor on the surface is evident by the appearance of the CH<sub>2</sub> and CH<sub>3</sub> stretching modes.



**Fig. 3** The surface bound motor (solid line) undergoes photoisomerization upon irradiation (365 nm, 0 °C) (dashed line). The reversion of the spectrum to the original indicates the thermal isomerization to the stable form (▲).

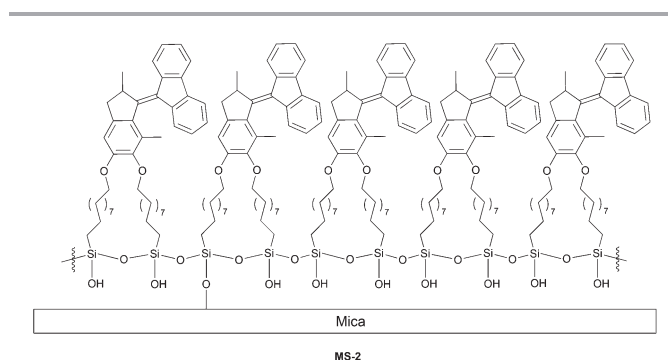
Finally, the UV-vis spectrum of the modified surface **MS-1** clearly shows the presence of the motor (Fig. 3, solid line), which compares well to the spectrum of motor **M1** (Fig. 1, solid line) in solution. The UV-vis spectrum of **MS-1** shows that the surface-bound motors undergo photochemical isomerization when irradiated with UV-light ( $\lambda_{\text{max}} = 365$  nm, 273 K, 45 min) (Fig. 3). The initial spectrum is recovered after warming the sample to room temperature. The changes in the absorption spectrum are similar to that observed for **M1** in methanol solution (365 nm, 253 K, 90 min) (Fig. 1) indicating that the rotary function is preserved when attached to the surface.

### M2 on mica

A considerable challenge in the area of molecular machines is to mechanically move adsorbates on top of a layer of responsive molecules.<sup>37–40</sup> In order to achieve the maximum mechanical effect, externally induced geometrical changes of the organic surface should be exploited equally. Substrates with atomically flat surfaces are considered to be ideal because it is uncertain how surface roughness affects the propensity for chemical conformational changes at an interface to induce motion in an adsorbate. Rougher areas may act as “road-blocks” that inhibit motion. Furthermore, application of solid surfaces with high roughness makes the visualization of adsorbed material (*e.g.*, macromolecules) with AFM more difficult and ambiguous. The importance of surface-flatness was demonstrated in the visualization of stretched DNA by AFM.<sup>41</sup>

To distinguish the adsorbate from the SAM, a smooth monolayer on an atomically flat surface is ideal. Mica provides an atomically flat surface that is step-free on a macroscopic length scale. It is well-established that alkyl-silanes can easily self-assemble on glass, silicon oxide and metal oxide surfaces by reaction and covalent-bond formation with the hydroxylated surface.<sup>31</sup>

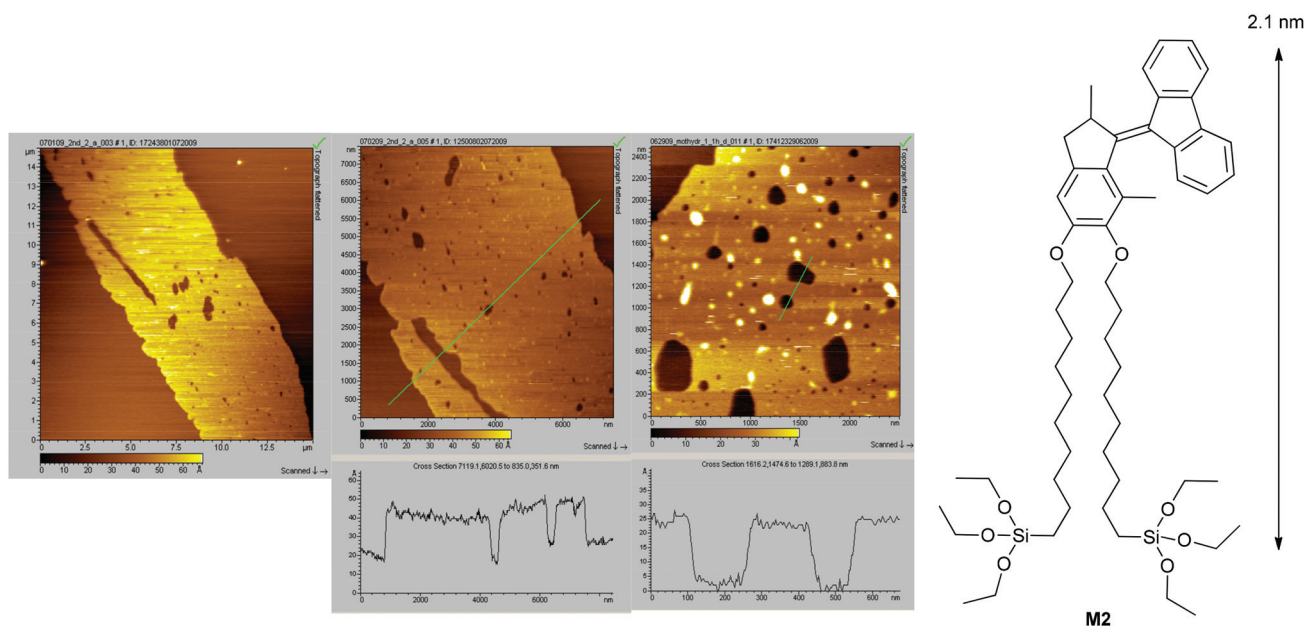
Controlling self-assembly on mica, however, is challenging because its surface is almost entirely non-functional;<sup>42</sup> there are few hydroxyl functionalities to provide a robust anchor. It is believed that silane monolayers adhere to mica through the formation of two-dimensional oligomeric/polymeric species in solution which anchors through adventitious Si–OH functionality.<sup>32,43,44</sup> **M2** was self-assembled on mica (Fig. 4) using a procedure similar to its self-assembly on quartz and Si<sup>32,45</sup> (see the Experimental section).



**Fig. 4** Schematic representation of a layer of motor **M2** on a mica surface. The surface of mica is almost entirely devoid of Si–OH functional groups. It is believed that silane monolayers adhere through the formation of two-dimensional oligomeric/polymeric species in solution which anchors through any adventitious surface Si–OH functionality.

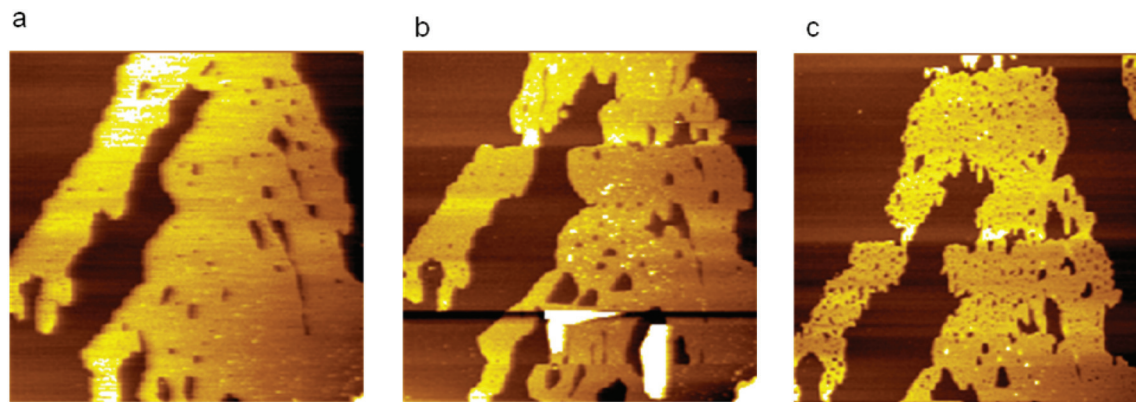
A detailed spectroscopic analysis of the film structure is more difficult in comparison to Si substrates. However, the atomically flat nature of the mica surface makes it ideal for AFM studies.<sup>46</sup> AFM tips with a force constant of 5 N m<sup>−1</sup> were used. The use of tips with higher force constants damaged the films, indicating the fragility of the physically adsorbed films. Similar observations have been previously reported.<sup>47,48</sup> Representative AFM pictures are shown in Fig. 5. It can be seen that the silane-containing motor molecules self-assemble to form micrometer sized carpets on mica. The thickness of the carpets is 2–2.5 nm, which is close to the ellipsometric thickness obtained for **MS-1**.

The formation of such condensed domains is consistent with the deposition, diffusion and aggregation (DDA) model described for similar systems.<sup>47,49,50</sup> Polymeric/oligomeric species and individual molecules adsorb onto mica from solution and can easily diffuse on the surface in order to aggregate with already deposited islands, since almost no covalent links form that could limit their mobility. In contrast to the uniform growth observed on the silanol rich silicon surface,<sup>51</sup> initial film growth on mica is primarily through diffusion-limited aggregation (resulting in island formation throughout the surface) while after longer immersion times the growth is limited by adsorption from solution (filling the pinholes and uncovered surface areas between the islands). Although the two growth mechanisms are mostly attributed to the presence or the lack of surface silanol groups, it has been reported that the two mechanisms may vary depending on the reaction conditions (*i.e.* low moisture content facilitates continuous growth while high water content facilitates the island growth mechanism).<sup>52,53</sup> The pinholes included in the monolayers have been observed previously and attributed to imperfect packing and monolayer reorganization processes.<sup>47,48</sup>



**Fig. 5** Representative AFM images of mica surfaces modified through the assembly of motor **M2**. Micrometer-sized carpets were found throughout the surfaces with 2–2.5 nm thicknesses, which are close to the estimated length of motor **M2**, indicating the presence of monolayer films.





**Fig. 6** AFM images show the effect of UV-irradiation (365 nm, rt) on motor film morphology on mica. Sample without irradiation; (a) sample after 35 min irradiation; (b) sample after standing overnight in the dark at rt. (c) (Image sizes are  $10 \times 10 \mu\text{m}$ .)

To test the film stability towards the effect of rotary motion, the mica surfaces were subjected to UV irradiation ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) (Fig. 6).

A sample (Fig. 6a) was irradiated for 35 min at rt. The AFM images show that after 35 min of irradiation changes in the film structure could be observed including the appearance of new pinholes and the broadening of existing pinholes (Fig. 6b). The samples were then left in the dark overnight (Fig. 6c). Images obtained after standing overnight show that the number of pinholes increased further and that the shape of the carpets changes.

It is obvious from the AFM images that irradiation initiates morphological changes in the motor film. The effect of the heat produced by the UV-lamp during irradiation could be excluded since post-baking at  $120^\circ\text{C}$  showed no considerable changes in the layer morphology. It is possible, however, that upon rotation of the rotor part of the motors the monolayer undergoes reorganization especially at the points where the cross-linking of the silane layer is incomplete.

Since the layers are not covalently attached to the mica surface, Si–O–Si bonding to the surface does not prevent structural reorganization. Comparable morphological conversions were observed in the case of azobenzene and azobenzene-containing polymer films on mica.<sup>54–57</sup> The morphology of the films was further altered after additional exposure to UV light (see ESI†). We attribute the morphological changes to photo-mechanical effects in the monolayer. Two effects are attributed to the persistence of morphological changes in the dark. The first is the thermal isomerization of the motor, which might affect intermolecular interactions in a manner similar to the photochemical isomerization. The second is that the photo-induced and thermally induced collisions between motors result in viscoelastic effects in the polysilane, which further disturbs the morphology of the surface-adsorbed monolayers.

## Conclusions

A disilane terminated molecular motor was synthesized and self-assembled on  $\text{SiO}_2/\text{Si}$ , quartz and mica surfaces.

Spectroscopic studies show that the motor retains its ability to undergo rotary motion when attached to a surface. AFM images of mica sheets immersed in self-assembly solutions show the presence of molecular “carpets” extending several microns. Irradiation of the “carpets” results in morphological changes.

## Experimental section

### Synthesis

For the characterization of intermediates in the synthesis of **M1** and **M2** see ESI.†

### Preparation of substrates

Silicon wafers (Wafer World Inc.) containing a thin layer of  $\text{SiO}_2$  (approximately 2 nm, exact value measured for each sample using ellipsometry) and quartz microscope slides (UQG Optics) were cleaned prior to use for 1 h using a 3 : 7 ratio of  $\text{H}_2\text{O}_2$  (30%) in  $\text{H}_2\text{SO}_4$  (‘piranha’) at  $>90^\circ\text{C}$ . (**Caution!** *This mixture is extremely corrosive and reactive towards organics.*) These samples were then rinsed with double distilled water (3 times) and with methanol and dried under a stream of argon. Clean mica surfaces were prepared by cleaving the top layer by covering with scotch tape and peeling off the layer.

### Preparations of **M2** films

Motor films were prepared following the procedure described in the literature.<sup>32</sup> 1.25 mL of a hydrolysis solution containing 12 mg disilane motor **M2**, 6 mL distilled THF, 31  $\mu\text{L}$  double-distilled  $\text{H}_2\text{O}$  and 4  $\mu\text{L}$  37% aq. HCl was added to 25 mL cyclohexane to give a slightly hazy solution. Piranha cleaned silicon wafers and quartz slides were immersed in this solution. In the case of mica the best results were obtained when the concentration of motor **M2** was 0.1 mM in the hydrolysis solution. In general quartz slides and silicon wafers were left immersed overnight, mica sheets were left immersed for 1 h. After the assembly, quartz slides and silicon wafers were rinsed and sonicated in DMF, toluene and MeOH for 2 min each and dried under a stream of Ar. Mica sheets were immersed briefly

in distilled toluene and post-baked at 120 °C for 1 h. Leaving out the post-baking step, however, was not considerably affecting the obtained results.

### Characterization of surfaces

Contact angles were measured under ambient conditions on a Data Physics contact angle goniometer. The contact angle was calculated using software provided by the company. The contact angle was measured in at least three different locations on each surface and the results averaged. Spectroscopic ellipsometry measurements were performed on a J.A. Woollam VASE ellipsometer. ATR-IR spectra of the surfaces were obtained using a Spectrum 400 FT-IR (Perkin Elmer) equipped with a Pike Veemax II attachment and a liquid nitrogen cooled MCT detector. Spectra were taken with parallel-polarized light and an incident reflection angle of 65° while samples were in intimate contact with a germanium crystal. Background spectra were taken on Si wafers containing an SiO<sub>2</sub> overlayer exposed to piranha solution in the same manner as the chemically modified samples. Samples were cleaned with lens tissue immediately before measuring. UV-vis absorption spectra were obtained using a V-630 spectrophotometer. AFM images were obtained with a PicoScan LE (Molecular Imaging) atomic force microscope in tapping mode. Tips with a force constant of 5 N m<sup>-1</sup> were used. Images were scanned at rates ranging from 1 to 2 lines per second.

### Acknowledgements

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